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GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 158251 dated 13th October, 1982.

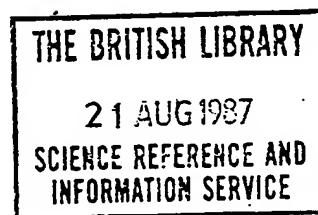
Application No. 754/De1/1982. dated 13th October, 1982.

Acceptance of the complete specification advertised on 4th October, 1986.

Index at acceptance - 32F, [IX(1)].

International Classification— C07c 21/18.

"A PROCESS FOR THE PRODUCTION OF TETRAFLUOROETHYLENE".



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The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

PRICE : TWO RUPEES

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This invention relates to a process for the production of tetrafluoroethylene. In particular, this invention relates to a process for the production of tetrafluoroethylene by the pyrolysis of monochlorodifluoromethane.

It is generally known that tetrafluoroethylene is monomer which, when subjected to the step of polymerization products polytetrafluoroethylene. The pyrolysis of monochlorodifluoromethane to obtain tetrafluoroethylene is generally known in the art. One such method consists in the pyrolysis of monochlorodifluoromethane at a temperature of between 600 to 850°C. It has been found that a pyrolysis does not initiate when employing a temperature below 600°C. Simultaneously, if a temperature higher than 850°C is employed in the step of pyrolysis, then undesired or degraded products are formed. Accordingly, in such a known process, the step of pyrolysis is carried out at a temperature of between 600 to 850°C. Several distinct disadvantages are associated with such a known process. One such disadvantage is that of a low efficiency and conversion. Yet another disadvantage is that the step of pyrolysis is effected in a platinum tube due to the formation of corrosive products, such as hydrochloric acid, in conjunction with tetrafluoroethylene.

In order to obviate such a disadvantage, it is known to incorporate a diluent such as nitrogen or hydrogen to monochlorodifluoromethane, and which is then subjected to the step of pyrolysis at a temperature of between 600 to 850°C. It has been found that such an addition of a diluent does increase the conversion in comparison to the process where the step of pyrolysis is effected in the absence of a diluent. However, a disadvantage associated with such a process is that of separating the TFE from the diluent.

Yet another process is known in the art and which employs steam as the diluent. In such a process, three to nineteen moles of steam per mole of monochlorodifluoromethane is employed for the reaction and which is subjected to the step of pyrolysis at a temperature of between 600 to 850°C.

An object of this invention is to propose an improved process for the production of TFE.

Another object of this invention is to propose a process for the production of TFE and which has a high yield.

Still another object of this invention is to propose a process for the production of TFE which is efficient.

Yet another object of this invention is to propose a process for the production of TFE from monochlorodi-

fluoromethane which no longer requires a reaction tube made of platinum or silver.

A further object of this invention is to propose a process for the production of TFE and having an absence or negligible amount of high boilers.

According to this invention there is provided a process for the production of tetrafluoroethylene from monochlorodifluoromethane which comprises in subjecting a reaction mixture of monochlorodifluoromethane and a diluent consisting of steam to the step of pyrolysis, recovering TFE therefrom characterized in that the reaction mixture is first subjected to a step of removal of oxygen therefrom by preheating the reaction mixture prior to the step of pyrolysis and then subjected to the step of pyrolysis.

In accordance with this invention, a reaction mixture is first prepared by adding a diluent to monochlorodifluoromethane. In accordance with a preferred embodiment of this invention, but without implying any limitation thereto, the diluent consists of steam and, wherein, upto 3 moles of steam is added to each mole of monochlorodifluoromethane. Thus, a steam of monochlorodifluoromethane is introduced into a bath of hot water to form the said mixture. The water is maintained at a temperature of between 80 to 97°C and the steam to monochlorodifluoromethane molar ratio being 1:1 to 3:1. It has been found that if such a molar ratio increases, then hydrolysis would set in and which is an undesired factor.

Reference is made hereinabove to the introduction of mfm into a bath of water at an elevated temperature and which functions as a diluent. The advantage of forming a reaction mixture in such a manner is that the molar ratio of the diluent to mfm is smaller than that known in the art. Even using smaller dilution ratio of diluent to mfd, higher conversion and higher efficiency can be achieved at very low contact times. Thus, making the process more economic in terms of plant size, for production of steam and for cooling of steam in gases coming from the reactor.

The next step in the process consists in preheating the reaction mixture. In accordance with this invention the reaction mixture, is introduced into a preheater having an agent for removal of oxygen. By way of example and without implying any limitations thereto, the agent consists of copper turnings. Thus in accordance with this invention the reaction mixture is introduced into a preheater having copper turnings therein, said preheater being maintained at a temperature of 300 to 425°C. Preferably, the temperature of the preheater is between 350 to 400°C. It has been found that the copper turnings at the operating temperature of 300 to 425°C reacts with the oxygen present in the reaction mixtures and becomes copper oxide. Reference is made herein to a removal of oxygen, it being understood that such a removal being complete or substantial. An advantage

derived by a complete or substantial removal of oxygen is that if oxygen is allowed to remain in the step of pyrolysis, then the presence of oxygen helps in the splitting of hydrofluoric acid and carbon dioxide.

In accordance with a preferred embodiment of this invention, the reaction mixture is introduced into the preheater and subjected to the said temperature. However, and in accordance with another embodiment of this invention, the diluent and mcd may separately be subjected to heating in the presence of said agent and only, thereafter, formed or mixed into a reaction mixture having oxygen removed therefrom. Similarly, and in accordance with yet another embodiment of this invention, the diluent and mcd may separately be introduced into the preheater in accordance with the aforesaid molar ratio and such that the formation of the reaction mixture and a removal of oxygen from the reaction mixture is effected in said preheater.

As described hereinabove, the step of preheating is carried out at a temperature of between 300 to 425°C. If a temperature less than 300°C is employed for the step of preheating, then copper does not act to form copper oxide. Simultaneously, if the temperature for the preheating step is greater than 425°C, then a pyrolysis may take place in the preheater, and which is not a desired factor.

The next step in the process consists in subjecting the reaction mixture to the step of pyrolysis. Such a step of pyrolysis is carried out in a manner known as such in the art. However, a distinction between the process of the prior art and that of the present invention resides in that the step of pyrolysis can suitably be carried in a pyrolysis tube consisting of nickel or an alloy of nickel. In the process of the prior art, such a pyrolysis was carried out in a platinum tube and which did contribute to the end cost of the process. As the process of the present invention does not allow a generation or formation of degraded or other undesired compounds of TFE and which boils at a temperature higher than TFE, the pyrolysis tube can now consist of nickel or nickel alloy.

Reference is made herein to a preheater and a pyrolysis tube. The residence time for the step of pyrolysis is between .006 seconds to 0.15 seconds.

Further objects and advantages of this invention will be more apparent from the ensuing examples, but which are not to be construed in a limited or restrictive manner.

EXAMPLE 1:

Monochlorodifluoromethane was passed through water heater at 20-90°C to get a steam of monochlorodifluoromethane in 1:1 molar ratio, the mixture was passed through preheating containing copper turnings at 380°C and then through a tubular reactor of nickel which was heated

electrically to 550-850°C, temperature was controlled by automatic temperature controller. The pyrolysed gases were immediately cooled by passing through a heat exchanger and samples of gas mixtures were analysed. Similarly other experiments were done at different contact times. Results are given in Table No. 1.

EXAMPLE-2:

Monochlorodifluoromethane was passed through water heated at 80-97.5°C to get a mixture of steam and monochlorodifluoromethane in 3:1 molar ratio. Mixture was preheated in a preheater containing copper turnings at 380°C and then pyrolysed in nickel tubular reactor at 200°C and 3.0×10^{-2} sec contact time. The conversion increased from 37.4% as in Example-1 to 23.0% under similar conditions of temperatures and contact times.

EXAMPLE - 3:

A mixture of steam and monochlorodifluoromethane in 3:1, was preheated in a preheater containing copper turnings at 380°C and the pyrolysed at 750°C for 5.9×10^{-2} sec. contact time in a nickel tubular reactor. The pyrolysed gases were immediately cooled by passing through heat exchanger and finally scrubbed in water at ice temperature. The acid found was analysed volumetrically at end of the reaction conversion calculated. Under the above conditions conversions was found to be 65%.

EXAMPLE-4:

Example 3 was repeated but preheater containing copper turning was replaced by a preheater of steel, under identical conditions of example 3 conversion calculated from acid analysis was found to be 58%.

In ~~an~~ copending patent application no 752/DEL/82 there is described a process for the production of tetrafluoroethylene from monochlorodifluoromethane which comprises subjecting monochlorodifluoromethane to the step of pyrolysis characterized in that monochlorodifluoromethane is first subjected to a step of removal of oxygen by preheating the reaction mixture in the presence of copper turnings and then to the said step of pyrolysis.

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TABLE-1.

Effect of temperature and contact time on pyrolysis of monochlorodifluoromethane in presence of one mole of steam using copper in the preheater.

Temperature °C	Contact time sec. ($\times 10^{-2}$)	Conversion.
650	2.9	3.6
650	5.8	6.2
650	8.7	8.2
700	2.9	8.5
700	5.8	13.0
700	8.7	40.0
700	14.7	59.1
750	0.84	6.0
750	3.0	10.4
750	5.8	26.0
750	8.7	47.9
750	14.7	76.5
800	0.84	23.9
800	3.0	37.4
800	5.8	40.9
800	8.7	48.6
800	14.7	72.2
850	0.84	36.0
850	3.0	46.1
850	5.8	78.0
850	8.7	77.5
850	14.7	72.4

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WE CLAIM :

- 1) A process for the production of tetrafluoroethylene from monochlorodifluoromethane which comprises in subjecting a reaction mixture of monochlorodifluoromethane and a diluent consisting of steam to the step of pyrolysis, recovering TEE therefrom characterized in that the reaction mixture is first subjected to a step of removal of oxygen therefrom by preheating the reaction mixture prior to the step of pyrolysis and then subjected to the step of pyrolysis.
- 2) A process as claimed in claim 1 wherein the step of preheating is carried out in the presence of copper turnup at a temperature of 300 to 425°C.
- 3) A process as claimed in claim 2 wherein the step of preheating is carried out at a temperature of 350 to 400°C.
- 4) A process as claimed in claim 1 wherein the step of pyrolysis is carried out in nickel or nickel alloy tube.
- 5) A process as claimed in claim 1 wherein said step of pyrolysis is carried out for a period of .006 to 0.15 secs.
- 6) A process for the production of tetrafluoroethylene from monochlorodifluoromethane substantially as herein described.

Dated this the 13th day of October, 1982.

Sd/-
(S.K. DUTT)
of L.S. DAVAR & CO.,
APPLICANTS' ATTORNEY.